

To: Rotola, Joe[Rotola.Joe@epa.gov]
From: Rotola, Joe
Sent: Thur 1/11/2018 8:00:12 PM
Subject: FW: Short-chain per- and polyfluorinated substances (PFASs)

From: Magriples, Nick
Sent: Thursday, December 28, 2017 3:29 PM
To: Rotola, Joe <Rotola.Joe@epa.gov>
Subject: Short-chain per- and polyfluorinated substances (PFASs)

Due to the phase-out of PFOA and the longer-chain fluorinated compounds, industry started to manufacture short-chain fluorinated compounds to use in their place. In the case of Dupont, that occurred around 2009/10. It should be noted that some of these short-chain compounds, as is reportedly the case with GenX and Dupont in North Carolina, may have existed as by-products 30 years earlier. The new compounds generally have lower molecular weights, are more soluble (>100x in the case of GenX compared to PFOA), shorter half-lives in humans and are not biodegradable. Several studies suggest some of the replacement PFASs may or may not be less hazardous than their long-chain predecessors, although publicly available information for most of the replacements is limited.

According to the North Carolina Department of Health and Human Services (NCDHHS), who is working in conjunction with EPA and CDC to update their risk assessment of GenX for the situation in Cape Fear, animal studies demonstrate liver and red blood cell non-cancer effects and pancreas, liver, and testicular cancer effects. Treatment processes used to remove these chemicals from water may not be as effective as with longer-chain PFAS. Limited studies indicate that it is more difficult to remove using carbon treatment, maybe due to the increased solubility.

The NCDHHS initially established a safety threshold of 71,000 ppt for GenX but more recently (July 2017) reevaluated their risk assessment with EPA's assistance to change the threshold to 140 ppt based on non-cancer effects to bottle-fed infants. The Governor has written a letter to EPA Administrator Pruitt asking to finalize the health assessment of GenX and has requested a public health assessment from the CDC. According to the Brunswick County Public Utilities, who contracted with Black & Veatch this past summer to evaluate alternatives for GenX and other PFAS treatment, there currently is very little information available on filtration at the utility or residential level that is known to remove GenX. The Black and Veatch draft study reviewed GAC, ion exchange, reverse osmosis and nanofiltration.

Some of the other well-known substitute fluorinated replacement chemicals for PFOA/PFOS besides GenX (CAS No. 62037-80-3), aka **2,3,3,3-tetrafluor-2(heptafluoropropoxy) propanoic acid /or/ perfluoro-2-propoxypropanoic acid**, made by Dupont/Chemours, include:

- 1) ADONA (CAS No. 958445-44-8), aka **3H-Perfluoro-3-[(3-methoxy-propoxy)propanoic acid]**, made by 3M
- 2) (CAS No. 908020-52-0), aka **perfluoro[(2-ethyloxy-ethoxyacetic acid)]**, made by Asahi
- 3) (CAS No. 329238-24-6), aka **perfluoro acetic acid, α -substituted with the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropoxy groups**, made by Solvay

There reportedly are also numerous companies in Japan, Europe and China that are manufacturing their own versions of these chemicals.

There are some good reports out of Europe (Netherlands, Denmark and Sweden) that provide some insight into these compounds. The listing (at the bottom of this email) of PFAS compounds found on the global market as of 2015 are extracted from a Swedish Chemicals Agency report. It is believed that the actual number of PFAS compounds may be as high as twice as many as the total in the listing below. This same document also contains information, which I have not attached, that associates short-chain compound use with types of manufacturing operations (at last in Sweden).

As for analytical, there are labs that are analyzing for GenX and a few short-chain perfluoro compounds. The Brunswick Water Authority in North Carolina used **Northern Lake Service, Inc.** to run Solid Phase Extraction LC/MS/MS with Method 537 standards. It appears that the only difference in the scan from what we have seen in the past is the GenX, with a level of detection of 0.73 ppt and a level of quantitation of 2.3 ppt. Other labs that provide this analysis include: **Pace Analytical Services** (standard 537 list with a couple short-chain compounds, GenX, and a couple of perfluorooctanesulfonamidoacetic acids), **GEL Laboratories** (includes 24 per- and poly-fluorinated compounds achieving detection limits below 5 ng/L), **SGS North America** (includes the standard list, GenX, a couple of shorter carboxylic acids and a longer series of sulfonate based perfluoro and fluorotelomer compounds), **ALS Environmental** (generally similar to SGS), **Eurofins Eaton Analytical** (generally similar to SGS, they have run samples for GenX and

ADONA at Cape Fear) and **Test America-Denver** (also offers a new method identified as PFAS Total Oxidizable Precursor (TOP) Assay). The compounds covered in the Cape Fear Study by Sun, et al., which appear to have been run by or through **NERL**, had fewer of the standard long-chain compounds in the typical Method 537 method and contains four mono-ether PFECAs (including GenX) and three multi-ether PFECAs, as well as two of the shorter chain PFCAs.

Without knowing the chemicals and their constituents used at the plant(s), sampling may not necessarily cover the additional compounds that potentially could be present. A supplemental 104e to St. Gobain requesting info on the chemicals it has been using since PFOA usage ended, including the name of the manufacturer and when the changeover occurred, may provide some insight that could potentially help to target the analytical. If the name of the product being used has not changed (i.e, Teflon dispersion), which reportedly has been the case with some products in general, then the request should also cover the specifics on the changed formulation, which may lead us to the manufacturer (and CBI). The original 104e response from St. Gobain indicates that they participated in the phase out of PFOA since 2003 by purchasing raw materials with decreasing levels of PFOA. I believe they continued to use it till around 2014. There had to be replacement product(s).

Chemical grouping of PFAS found on the global market and the number of different substances in each group.

<u>Fluoro group</u>	<u>Number of substances</u>
fluorinated (meth)acrylate polymers	234
N-alkyl perfluoroalkyl sulfonamides	226
poly/perfluorinated polymers	173
poly/perfluorinated phosphoorganics	143
polytetrafluoroethylene (PTFE)	137
poly/perfluorinated alkanes/alkenes	120
poly/perfluorinated sulfonic/sulfinic acids	93
poly/perfluorinated carboxylic acids	93
other poly/perfluorinated organics	90
poly/perfluorinated ethers	80
poly/perfluorinated esters	69
poly/perfluorinated alkanoyl/sulfonyl chloride or fluorides	68
poly/perfluorinated iodides	64
poly/perfluorinated (meth)acrylates	58
poly/perfluorinated alcohols	56
poly/perfluorinated sulfonamides	52
poly/perfluorinated siloxanes/silicones/silanes/silicates	50
poly/perfluorinated thiols	45
poly/perfluorinated copolymers	35
fluorinated urethanes polymers	33
poly/perfluorinated amines	34
polyfluoro siloxane and silicone polymers	29
poly/perfluorinated ammonium organics	21
poly/perfluorinated naphthalenes	16
poly/perfluorinated oxiranes	14
poly/perfluorinated ethoxylates	8
fluorinated oxetane polymers	8
poly/perfluorinated iodides	4
poly/perfluorinated urethanes	3
perfluoroalkyl sulfonamides	2
polyvinylidene fluoride (PVDF)	2
Total number = 2,060	